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Critical points of condensation in Coulomb systems

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<u>Abstract.</u> The critical points of condensation in Coulomb systems are described here by a modified van der Waals equation of state taking into account a many-particle exchange interaction between virtual atoms with overlapping classically accessible spheres of valence electrons. A characteristic feature of the Coulomb critical points is strong electron – ion coupling caused by the proximity to the metal – insulator transition. We consider a cell model of the exchange interaction of virtual atoms and examples of Coulomb critical points in a system of charged hard spheres, in alkali metals, in metal – ammonia solutions, and in excitonic systems. The Coulomb critical point parameters of transition metals are determined. We consider examples of insulator – metal transitions in semiconducting and dielectric fluids which form the Coulomb systems only in the liquid phase, and discuss a semiconducting critical state of mercury.

1. Introduction

The Coulomb interaction is so fundamental that its limited role in the theory of condensation seems astonishing. Indeed, below the critical temperature even metals and ionic melts

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have a weakly ionized gas phase consisting mainly of neutral atoms or molecules. The appearance of a neutral structure in a Coulomb system is easily demonstrated with classical charged hard spheres modelled by the Monte Carlo method. Numerical simulations show that at sufficiently low temperatures the gas phase is divided into Bjerrum pairs composed of coupled spheres with opposite charges. Similarly to polar molecules, at long distances the Bjerrum pairs attract each other via dipole – dipole rather than the Coulomb interaction. However, due to the high density there is a residual Coulomb interaction near the critical point, since the spheres of ion motion in the Bjerrum pairs overlap giving rise to an ion exchange. Analogously, near the liquid - gas critical points of metals a many-particle exchange interaction of virtual atoms with overlapping classically accessible spheres of valence electrons can be considered. We refer to such critical points as Coulomb or plasma critical points.

The problem of plasma critical points goes back to Ya B Zel'dovich and L D Landau [1] who noticed the possibility of two (except unlikely coincidence) qualitatively different phase diagrams of metals. In the first case, near the critical point the vapor becomes metallic under compression before the condensation line. There are two coexisting metallic phases in this region, i.e. metallic liquid and metallic gas. Otherwise, in the second case near the critical point both phases are dielectric. As has now been experimentally confirmed, mercury belongs to the second case. The transition point determined by extrapolating the conductivity activation energy to zero [2], and by the Knight shift [3] is at one and a half the critical density, whereas near the critical point mercury behaves as a semiconductor with an energy gap of about 3 eV and, correspondingly, a low conductivity. Although, in the early work, Zel'dovich and Landau supposed the insulator – metal transition to be a first-order phase transition, the experiment unambiguously shows that the transition is continuous, i.e. is not accompanied by any discontinuity in the thermodynamic values.

In contrast, alkali metals at the critical points have a minimum metallic conductivity [4], therefore their phase diagrams should be referred to the first case. Although the first experiments in caesium and rubidium allowing such a conclusion were carried out in the middle of the seventies, they could not be correctly interpreted within the framework of the theory of nonideal plasma with a weak electron – ion interaction. One of the basic difficulties in this theory is the problem of full ionization of caesium at the critical temperature of about 2000 K. We note that in the early review on nonideal plasma by Norman and Starostin [5] the degree of ionization at the critical point of caesium was estimated to be as small as 10^{-4} . The close connection between the critical points of alkali metals and a plasma phase transition with two metallic phases was first evidenced by the author [6].

The subjects of the present paper are closely associated with the review on gaseous metals [7] published eight years ago. However, special attention will be paid here not to the electron properties, but to the equation of state describing the Coulomb critical points of metals and of a wider class of systems. The insulator – metal transition is considered mainly to specify the phase diagram and the nature of the critical points of particular systems. The outline of the paper is clear from the contents. Section 2, a general review of the problem, contains examples of experimentally known plasma phase transitions. The systematic consideration begins with a model classical system of charged hard spheres which allows the essential aspects of the problem to be presented. Then we proceed to the analysis of electronic systems based on quantum concepts.

2. Plasma phase transition

After the pioneering paper by Zel'dovich and Landau [1], the possibility of Coulomb condensation was studied within the framework of the theory of nonideal plasma, not yet restricted to metals (see the review by Norman and Starostin [5]). Later works are cited in the book by Kraeft et al. [8] and the recent review by Redmer [9]. In this section we only briefly touch these works paying special attention to the most recent of them, and enumerate those systems in which Coulomb condensation seems most probable, if not well established.

With a vanishing derivative of the pressure with respect to the volume, the Debye–Hückel theory already gives an indication that plasma condensation is possible. However, the zero of the derivative is far beyond the limits of applicability of this theory describing weak Coulomb interaction, and does not correspond to any real transition. The same situation remains in higher orders of an asymptotic expansion of thermodynamic quantities in the plasma interaction parameter.

Formally, plasma condensation also appears in a model of strongly coupled ions embedded in an ideal degenerate electron gas of high density [10]. This one-component plasma model was originally used for meeting the conditions which occur in astrophysics in white dwarfs and properly describes the crystallization of ions in a weakly polarizable electron gas. However, the one-component plasma model is inadequate for the description of condensation because of the metal– insulator transition near the critical density. The problem does not become clearer for Padé approximations connecting opposite asymptotics of low and high densities. For this reason, the plasma phase transitions are usually discussed as hypothetical [8, 9].

In the case of strong coupling, a partially ionized plasma consists of atoms and free electrons and ions which still form overlapping electron—ion pairs or virtual atoms. The electron energy includes the internal energy of virtual atoms and the interaction energy between virtual atoms. The minimum internal energy of virtual atoms corresponds to a boundary in the energy spectrum, which separates virtual and normal excited atoms. The attitude of this boundary, which determines the percolation lowering of the ionization potential, essentially influences the degree of ionization. However, the variations due to the shift of the end-point energy are exactly compensated in the sum of contributions of normal and virtual atoms, the full thermodynamic functions being not explicitly dependent on this boundary.

The last statement establishes an important principle [7] from which it follows that only interactions between virtual atoms but not intraatomic interactions contribute to the equation of state. By this principle, the equation of state of virtual atoms is the same as in the case of full ionization caused by the insulator – metal transition. In the vicinity of this transition, the ground atomic states also overlap, therefore the system consists only of virtual atoms. Obviously, in this case the ordinary scheme of partial ionization with a different description of bound and free electrons makes no sense.

In the vicinity of the insulator-metal transition, the ordinary scheme of partial ionization remains unsatisfactory even taking into account the polarization interaction between charged and neutral particles, which may strongly increase the degree of ionization. For example, the estimates of the critical pressure for caesium and rubidium, based on this scheme [9], are several times greater than the experimental values. Besides, this scheme with the realistic interaction between neutral particles yields a weak first-order phase transition creating a small density gap in the range of metallization in liquid hydrogen [11]. However, it would contradict the conclusion that the insulator-metal transition is continuous, which follows from detailed studies of such a transition in mercury.

A general feature of Coulomb critical points, caused by the proximity to the transition into a neutral fluid, is strong electron-ion coupling. In this connection, another description of the metal critical state originated from the electron theory of condensed matter. Hernandez et al. [12, 13] utilized a model of a lattice gas of ions, describing the electron states in the tight-binding approximation (or a model of narrow bands). In contrast to this scheme more appropriate for solids, we consider a fluid of overlapping virtual atoms with partially free electrons and calculate their interaction energy using a Wigner-Seitz cell model [14, 15]. The advantage is that this model is more closely connected with plasma theory, and in a considerably smaller degree with the crystalline lattice which has no relevance to the critical point. For this reason, the model of virtual atoms will be considered in some detail.

Apparently, a number of base and transition metals besides alkali metals have Coulomb critical points [7]. Therefore, the theory has a rather broad range of applications. In particular, it becomes possible to calculate the parameters of the critical points of metals which are generally not accessible experimentally but estimated by extrapolating thermodynamic dependences from lower temperatures.

We further notice two other systems with phase transitions evidently having Coulomb critical points. The first is the well-known sodium – ammonia solution. A gap of solubility of sodium appears because of its partial condensation to a concentrated metallic phase. At the consolute point, the system has a minimum metallic conductivity [16] resulting from overlapping impurity states of sodium atoms in a dielectric medium [17]. It follows that near the consolute point the phase transition is caused by a many-particle exchange interaction between virtual impurity atoms.

The second is an exciton system in strongly excited semiconductors. The condensation of excitons forming a metallic electron-hole liquid [18] is an example of nonequilibrium phase transitions. The critical exciton density is estimated to be so high that excitons overlap, the condensation being determined by the exchange-correlation interaction between electrons and holes (see the review by Rice et al. [19] and references cited therein).

Thus, in a number of cases hypothetical phase transitions are probably an artefact of the approximate theory of nonideal plasma. However, a rather great number of known phase transitions can be referred to as plasma phase transitions near critical points.

3. Model of charged hard spheres

It is convenient to begin our consideration with a model problem of charged hard spheres, which reveals Coulomb condensation, in this case generally accepted. A system of hard spheres of diameter *d* having electric charges $\pm e$ (where *e* is the electron charge) is the simplest statistical model of ionic melts and electrolytes. The hard spheres are characterized by the packing factor $\eta = \pi d^3 n/6$, where *n* is the total number density of positive and negative ions. This classical system of charged hard spheres allows Monte Carlo simulation. Being well defined, this model is of importance for analyzing the properties of the many-particle system and, in particular, for testing approximate estimates of the Coulomb critical points.

Around each ion we construct a sphere of radius d as a locus for the center of another member of the Bjerrum pair with the binding energy $D = e^2/d$. We assume that these spherical shells overlap forming an infinite percolation cluster where positive and negative ions alternate as in the corresponding ionic lattice (Fig. 1). According to the triangle inequality, the distance between two nearest identical (to be definite, positive) ions belonging to the percolation cluster is smaller than 4d. Therefore, the potential barrier between the positive ions (with respect to a negative ion) is lower than -D. Due to the smoothing of a potential relief, the negative ion found between positive ions can transfer from one positive ion to another, i.e. between Bjerrum pairs. Thus above the percolation threshold of the shells the ions in the Bjerrum pairs are transient, and the system becomes a conductor with a hopping mobility of ions.

The percolation threshold of overlapping shells is not sensitive to the relatively small hard core or to the long-range interaction described by mean field theory. According to Monte Carlo simulations [20] for a hard core radius equal to half the shell radius, the threshold volume fraction of the shells is about 1/3 with the hard spheres taking ≈ 0.04 of the volume.



Figure 1. Charged hard spheres with overlapping shells.

Since the packing factor is rather small, the thermal pressure near the percolation threshold of the shells is described with good accuracy by the van der Waals formula with the fourfold volume of hard spheres excluded:

$$p_T = \frac{nT}{1-4\eta} \; ,$$

where p_T is the thermal pressure, and *T* is the temperature in energy units. The long-range Coulomb attraction is expected to be well described in a mean field approximation. The Coulomb energy of the Bjerrum pairs consists of the internal energy -ND/2, where *N* is the total number of ions, and the residual Coulomb interaction energy which has a Madelung form for strong ion correlation, $U = -\alpha e^2 N^{4/3}/V$, where α is the Madelung constant, and *V* is the system volume. Notice that separating the internal energy of the Bjerrum pairs we renormalize the ordinary Madelung constant for an ionic lattice. The Coulomb lowering of the pressure is obtained by differentiating the energy with respect to the volume, $\Delta p = -\partial U/\partial V$. The internal energy of the pairs does not contribute to the pressure, being independent of the system volume, therefore we obtain $\Delta p = -\alpha e^2 n^{4/3}/3$.

Collecting the terms, we arrive at a van der Waals equation for the system of charged hard spheres:

$$p = \frac{nT}{1 - 4\eta} - \frac{1}{3}\alpha e^2 n^{4/3} \,. \tag{1}$$

By solving Eqn (1) with the conditions $\partial p/\partial n = \partial^2 p/\partial n^2 = 0$, we obtain the critical parameters

$$T_{\rm c} = \frac{16}{49} \left(\frac{3}{14\pi}\right)^{1/3} \alpha D \,, \tag{2}$$

$$p_{\rm c} = \frac{1}{49} \left(\frac{3}{14\pi}\right)^{1/3} \frac{\alpha D}{2\pi d^3} \,, \tag{3}$$

$$\eta_{\rm c} = \frac{1}{28} \approx 0.036 \,.$$
 (4)

We note that the critical packing factor following from Eqn (4) is approximately ten times smaller than the packing factor in normal liquids, $\eta_n = 0.45$, found by fitting the main peak of the radial distribution function [21]. In modern Monte Carlo simulations, the critical packing factor is varied from 0.02 to 0.04, because the critical point cannot be reached (see the review by Fisher [22]). Therefore, formula (4) falls within the range of uncertainty. A high critical expansion, of the order of 10 compared to about 3 in neutral fluids, is distinctive of Coulomb systems.

Ionic systems generally form a simple cubic lattice with alternate positive and negative ions, which is described by the well-known Madelung constant. The renormalization of the Madelung constant can be carried out by directly excluding the internal energy of the Bjerrum pairs from the Coulomb interaction energy. In order to calculate the Coulomb energy, we use a principle of electric neutrality leading to cancellation of great terms with opposite signs. Setting a positive ion at the origin, we add together the potential energy of interaction of the central ion with six nearest negative ions at the distance $a = n^{-1/3}$, where a is the lattice constant, and with an equal number of positive ions at the distance $a\sqrt{2}$ in the next spherical layer. Obviously, repeating the procedure for a negative ion, another member of the Bjerrum pair, or symmetrizing in charges, we obtain the same result. Such a procedure suggests a minimization of the charge separation radius, which is apparently justified for liquids with even the second coordination sphere smeared out. The calculation gives the Coulomb interaction energy per positive ion

$$-6\left(1-\frac{1}{\sqrt{2}}\right)\frac{e^2}{a} = -1.75e^2n^{1/3}\,,$$

which practically coincides with the known value including the numerical coefficient [23]. Subtracting an energy corresponding to interaction with another member of the Bjerrum pair in the lattice model and assigning the residual interaction energy to the total number of ions, we obtain the renormalized Madelung constant

$$\alpha = \frac{1.75 - 1}{2} = 0.375.$$
 (5)

We note that the renormalized constant following from Eqn (5) is approximately 2.3 times smaller than the ordinary Madelung constant defined with respect to the total number of ions, i.e. 1.75/2.

Substituting the renormalized Madelung constant into Eqns (2) and (3), we find the critical temperature

$$T_{\rm c} = 0.05D$$
, (6)

and pressure

$$p_{\rm c} = 5 \times 10^{-4} \frac{D}{d^3} = 0.01 \frac{T_{\rm c}}{d^3} \,.$$
 (7)

Numerical modelling allows us to find the densities of liquid and gas phases as functions of the temperature, intersecting at the critical temperature $T_{\rm c} = 0.057D$ (but the critical pressure remains uncertain due to strong compensation of the thermal and Coulomb contributions [24]). The discrepancy between the theoretical estimate due to Eqn (6) and numerical experiments is only 12%. As we will see, such an accuracy is also typical for estimates of the critical points of alkali metals, which are known experimentally. Unfortunately, the critical points of ionic melts are hardly accessible that makes the direct comparison with experiment impossible.

By Eqn (4) the critical packing factor is somewhat smaller than the shell percolation threshold estimated above. Even if, as we suppose, the genuine critical density is greater, it must be rather close to the threshold. Taking into account the weak dependence of the pressure on the density near the critical point, the gas phase is found to lie below the percolation threshold of the shells almost over the whole phase equilibrium line $p_s = p_s(T)$. Supposing the gas phase consists of partially dissociated Bjerrum pairs and taking into account the Coulomb and dipole interactions, Fisher [22] could estimate the critical parameters. However, such an analysis is more appropriate for densities much smaller than the critical value.

As is known, the van der Waals equation does not take into account critical peculiarities caused by fluctuations. The question of critical behavior in Coulomb systems was considered by Levin and Fisher [25]. Though experimental information in electrolytes is still lacking, the difference between Coulomb and neutral systems does not seem so radical taking into account the virtual Bjerrum pair structure. Nevertheless, there exist some indications that in Coulomb systems the critical region with an essential deviation from the mean field theory decreases (see references in the cited paper by Levin and Fisher).

The problem of charged hard spheres gives the clearest and commonly accepted proof that Coulomb critical points exist. Although without explicit renormalization, the Madelung energy has already been used with some success in estimating the critical points of ionic salt melts [26]¹, and was discussed more recently by Levin and Fisher [25]². The equation of state of electrolytes presented above has been obtained from an analogous equation for plasma critical points of metals [27].

4. Percolation in atomic systems

Starting from this section, we turn to electronic systems with electron exchange between overlapping atomic shells, in contrast to the ion exchange between the Bjerrum pairs. Basically, the size of atomic shells is determined by the radius of classically accessible spheres of the valence electrons. Metallic plasma formed by overlapping atomic shells differs from the ionic systems in the quantum uncertainty of the electron coordinates described by the wave function. For example, the 6s valence electron state in a caesium atom has completely uncertain angular coordinates. Most probably, in this state the electron is located in a classically accessible sphere of radius $R_a = e^2/I$, where *I* is the ionization potential. This can be easily verified using an asymptotic Coulomb wave function [28]

$$\Psi(r) \approx \frac{2^{\nu} k^{\nu+1/2}}{4\pi \nu^{\nu+3} \Gamma(\nu)} r^{\nu-1} \exp(-kr) , \qquad (8)$$

where $k = (2mI/\hbar^2)^{1/2}$ is the inverse decay length, $v = (Ry/I)^{1/2}$ is the effective principal quantum number, $Rv = me^4/2\hbar^2$ is the hydrogen ionization potential, and $\Gamma(v)$ is the gamma function. Integrating the wave function squared, we find the probability of being outside the classically accessible spheres [29]:

$$P = \frac{\Gamma(2\nu+1,4\nu)}{2\nu^{2(\nu+3)}\Gamma^{2}(\nu)},$$
(9)

where $\Gamma(2v + 1, 4v)$ is the incomplete gamma function. In the case of caesium, this probability is only 0.2% (it increases to

¹ Because of a mistake in the integral expressing the potential within the uniformly charged sphere, the Madelung constant was twofold decreased being only 15% greater than its properly renormalized value. ² The author is grateful to M Fisher for the references.

23% with $I \sim Ry$ in nonmetallic elements). Therefore, the remainder ion in a metal atom is almost fully screened within the classically accessible sphere. Since radial motion with a great quantum number is quasi-classical, the main maximum of the wave function is attached to the classically accessible sphere, thus in a qualitative analysis an electron spreads over this sphere.

When classically accessible spheres overlap forming an infinite percolation cluster (Fig. 2), it becomes probable that virtual atoms in such a cluster exchange electrons. We first consider a pair interatomic repulsion with a small radius (the many-particle attraction between atoms will be considered somewhat later). We assume the directions of spins in the percolation cluster alternate, and correlations between electrons with opposite spins are negligible. Although the electron shells of two neighboring atoms overlap, the remainder ions inside remain screened. However, if ions enter the electron shell surrounding another ion, the ion potential is no longer compensated by the (constant) potential of the shell. Then an extra potential energy appears,

$$U(R) = \frac{z^2 e^2}{R} - z^2 I,$$
(10)

where $R \leq R_a$ is the distance between the atoms, and z is the valence (charge number) of remainder ions, introduced in the general case. On the thermal energy scale at low temperatures $(T \leq I)$, the potential U(R) is very steep, therefore the distance of closest approach of two atoms is approximately equal to R_a . This conclusion can be easily verified for the ground ¹ Σ term of alkali dimers [30] with the repulsive branch describing a pair interaction of atoms with opposite spins at small distances.

The interatomic repulsion at the distance R_a , caused by the bare Coulomb interactions of remainder ions, is modelled by considering atoms as hard spheres of diameter $d = R_a$. It can be directly verified that at normal densities in liquid alkali metals the packing factor of these hard spheres varies from 0.225 for caesium to 0.45 for lithium. When allowing for some



Figure 2. Percolation cluster of overlapping classically accessible spheres.

variation of the diameter in the hard sphere model with varying conditions, such values reasonably agree with the theory of liquids [21].

However, the above-neglected exchange repulsion of overlapping electron shells becomes more important or even determinative for polyvalent atoms with high ionization potentials. For example, in liquid mercury at normal density $\rho_n = 13.6 \text{ g cm}^{-3}$, the packing factor of hard spheres of diameter $d = R_a$ would be only 5%, i.e. too small for a stable liquid. This is an indication that the fluid density is really limited by the exchange repulsion with a radius exceeding the Coulomb repulsion radius of ions. Obviously, this is the reason why mercury becomes a semiconductor upon relatively small expansion. Digressing from the complexities caused by the molecular structure, this statement is relevant to arsenic, selenium and tellurium as well.

As was already mentioned, on approaching the percolation threshold, the volume of shells with relatively small hard cores is about 1/3 of the whole volume. Now, we consider this point in more detail. The relative volume of atomic shells is characterized by the parameter

$$\zeta_0 = \left(\frac{R_a}{R_s}\right)^3,\tag{11}$$

where $R_s = (4\pi n_a/3)^{-1/3}$ is the Wigner – Seitz radius, and n_a is the atomic number density. The packing factor of effective hard spheres with diameter $d \approx R_a$ is also expressed via this parameter:

$$\eta = \left(\frac{d}{2R_s}\right)^3 \approx \frac{\zeta_0}{8} \,. \tag{12}$$

We determine the mean coordination number in a percolation cluster, i.e. the number of atoms overlapping the one chosen at the cell center with their electron shells:

$$B = \frac{8(\zeta_0 - \eta)}{1 - 4\eta} \,, \tag{13}$$

where the van der Waals denominator describes the excluded volume for a small packing factor of the hard spheres. Expressing ζ_0 from Eqn (13) by *B* and η , we obtain

$$\zeta_0 = \frac{B}{8} - \eta \left(\frac{B}{2} - 1\right).$$
(14)

Substituting Eqn (12) into (14) and solving the equation at the percolation threshold with respect to ζ_0 , we find

$$\zeta_{\rm pc} = \frac{B_{\rm pc}}{8} \, \frac{1}{1 + (B_{\rm pc}/2 - 1)/8} \approx 0.325 \,. \tag{15}$$

In the last equation we substitute $B_{\rm pc} = 2.7$ for an ideal system of overlapping spheres [31], assuming that the threshold coordination number is an approximate invariant. As a result of compensation of two competing effects, the threshold in Eqn (15) is rather close to its value for an ideal system, $B_{\rm pc}/8 \approx 0.34$. Indeed, the presence of hard cores restricts the overlap of shells, thus decreasing the density necessary for percolation. On the other hand, the hard cores bound a coordination sphere for the centers of atoms overlapping with the central atom and in doing so they increase the required density. To complete the analysis we consider the percolation threshold of shells as a function of the relative radius of the hard core which is no longer fixed. In general, if the packing factor is not small, Eqn (13) is rewritten in the form

$$B = 8(\zeta_0 - \eta)F(\eta), \qquad (16)$$

where $F(\eta)$ is the Carnahan – Starling function describing the excluded volume [32]:

$$F = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \,. \tag{17}$$

Substituting $\eta = c^{3}\zeta_{0}$, where $c = d/2R_{a}$, and the threshold coordination number $B_{pc} = 2.7$ into Eqns (16) and (17), we obtain an algebraic equation which determines the function $\zeta_{pc}(c)$. This function practically coincides with the above-estimated threshold in Eqn (15) for c = 0.5 and is shown to agree with results of Monte Carlo simulations [20] in Fig. 3. With *c* increasing over 0.8, the threshold increases, and with *c* close to unity it goes to the random close packing $\zeta_{pc} = 0.64$.

In addition to the bare Coulomb repulsion between remainder ions modelled by hard cores, there is a manyparticle exchange attraction of virtual atoms in percolation clusters, described in a mean field approximation (see next section). Apparently, the attraction does not essentially influence the percolation threshold since due to averaging the interaction energy weakly depends on the atomic configuration.

5. Virtual atoms

In this section we will consider special properties of the system of overlapping atoms which form the percolation cluster. The notion of virtual atoms with weakly overlapping electron



Figure 3. Percolation threshold of shells versus the relative diameter of hard cores. Dots are resulted from Monte Carlo simulations [20].

shells suggests that the electronic state changes only a little. Nevertheless, the electronic state of virtual atoms qualitatively differs from that of isolated atoms. Since the classically accessible spheres of the valence electrons overlap, the atomic screening of the remainder ion becomes collective, thus mixing the ground atomic state with the asymptotically free motion in a screened potential. Therefore, virtual atoms possess a continuous spectrum of electronic excitations. An adequate method of description of virtual atoms is provided by the density matrix in presentation of the eigenfunctions of the free atom, a_{mn} . In particular, the internal energy of the virtual atom, expressed by the density matrix, is given by

$$E = -a_{00}I + \sum_{n \ge 1} a_{nn}(-I + \varepsilon_n) + a_{pp}\varepsilon_p , \qquad (18)$$

where a_{00} and a_{nn} are the diagonal matrix elements, and ε_n the excitation energies of the atomic levels. A matrix element a_{pp} corresponds to asymptotically free motion with an excitation energy $\varepsilon_p = p^2/2m$, where p is an asymptotic momentum. Phenomenologically, this matrix element is determined by the condition that the energy ε_p of free motion plays the role of excitation.

Using the normalization condition

$$a_{00} + \sum_{n \ge 1} a_{nn} + a_{pp} = 1, \qquad (19)$$

we rewrite the internal energy defined by Eqn (18) in a more transparent form

$$E = -I(1 - a_{pp}) + a_{pp}\varepsilon_p + \sum_{n \ge 1} a_{nn}\varepsilon_n .$$
⁽²⁰⁾

From Eqn (20), the minimum internal energy E = -I corresponds to zero matrix elements $a_{pp} = a_{nn} = 0$, in accordance with the variational principle of quantum mechanics.

With the free-like excitation ε_p caused by screening, the minimum internal energy is then

$$E = -I + \varepsilon_p \,. \tag{21}$$

To put it otherwise, the last equation represents the energy spectrum of noninteracting virtual atoms.

Comparing Eqns (21) and (20) (with $a_{nn} = 0$), one obtains

$$a_{pp} = \frac{x}{1+x} \,, \tag{22}$$

where $x = \varepsilon_p / I$. Thus, the matrix element a_{pp} describing the low-energy excitations ($\varepsilon_p \ll I$) is small. The other matrix elements closely connected with the interatomic interaction cannot generally be determined.

The density of states of partially free electrons in virtual atoms, compared to that of free electrons, increases since the states belonging to different virtual atoms are distinguishable even though their wave functions overlap. One can distinguish between the electronic states of neighboring atoms during the transition time

$$\tau' = \frac{\tau}{\vartheta} \,, \tag{23}$$

where $\tau = R_s/v$ is the time of free flight, v = p/m is the velocity of free motion corresponding to the excitation

energy ε_p , and $\vartheta < 1$ is the localization factor just defined by Eqn (23). In particular, above the percolation transition the localization factor is [33]

$$\vartheta = \frac{3T/2 - \varDelta_{\rm pc}}{\varDelta_{\rm cp} - \varDelta_{\rm pc}} , \qquad (24)$$

where $\Delta_{pc} < 0$ is a (virtual) mobility gap, and $\Delta_{cp} > 0$ is a soft gap where the mobility is smaller than the minimum gaskinetic value. The gaps are given by formulas

$$\Delta_i = I - \frac{e^2}{R_i}, \quad i = \text{pc, cp}$$
(25)

with $R_{\rm pc}$ the percolation radius, and $R_{\rm cp}$ the close packing radius. At the critical points of alkali metals with an experimentally determined volume fraction of classically accessible spheres $\zeta_0 = 0.365$, the localization factor is estimated to be $\vartheta_c \approx 0.4$.

Virtual atomic states are defined for a finite transition time within a sphere of radius R_s/ϑ . In the approximation of free motion, the density of states is then

$$\frac{\mathrm{d}g}{\mathrm{d}p} = g_{\mathrm{a}} \frac{4\pi p^2 \Omega}{\left(2\pi\hbar\right)^3}\,,\tag{26}$$

where g_a is the statistical weight of the ground-state atom, and $\Omega = 1/n_a \vartheta^3$ is the volume of a sphere where the mixed states of virtual atoms are defined.

The Fermi energy of partially free electrons is renormalized in accordance with the density of states. Since the density of states increases proportionally to the volume ϑ^{-3} , the renormalized Fermi momentum decreases as ϑ , and the Fermi energy decreases as ϑ^2 , we obtain

$$\frac{\varepsilon_{\rm F}'}{I} = \left(\frac{9\pi\zeta_0}{16g_{\rm a}}\right)^{2/3} \frac{I}{\rm Ry} \vartheta^2 \,, \tag{27}$$

where the prime denotes the renormalized quantity. At the caesium critical point, the renormalized Fermi energy is approximately two times smaller than the temperature, therefore the Fermi correction to the pressure [34] is small. Basically, the degeneracy of partially free electrons depends on the localization factor and becomes prominent when this factor is close to unity.

Taking into account a quantum spreading of electrons in space, the energy of the residual Coulomb interaction can be estimated with a modified one-component plasma model excluding the internal energy of virtual atoms. In the case of strong interaction with a great coupling parameter, i.e.

$$\Gamma = \frac{z^2 e^2}{R_s T} \gg 1 \,, \tag{28}$$

this model is equivalent to an ionic cell model, the potential energy being

$$U = -\gamma n_a \frac{z^2 e^2}{R_s} , \qquad (29)$$

where γ is another Madelung constant. The γ is related to the coefficient α in the expression for energy $-\alpha z^2 e^2 n_a^{4/3}$ by an equality $\alpha = \gamma (4\pi/3)^{1/3}$. Assuming the valence electrons to be mainly distributed in a range from the ionic core radius R_c to

the cell radius R_s with a uniform probability density, calculation of the electrostatic energy reduces to a simple integration. Since the electron density belongs to diatomic quasi-molecules formed by the central atom and atoms in neighboring cells, we find that the renormalized interaction energy corresponds to half the total electrostatic energy of the cell. Thus, the interaction energy equals

$$U = -\frac{e^2 n}{2} \int_{R_c}^{R_s} \frac{z(r)}{r} \, 4\pi r^2 \, \mathrm{d}r \,, \tag{30}$$

where $n = zn_a/(1-b)$ is the electron density, $b = (R_c/R_s)^3$ is the volume fraction of the ionic core where the valence electron density is small, and z(r) is a screened ionic charge:

$$z(r) = z - \frac{4\pi n}{3} (r^3 - R_c^3), \quad r > R_c.$$
(31)

Calculation of the integral in Eqn (30) leads to formula (29) with a Madelung constant

$$\gamma = \frac{0.9 - 1.5b^{2/3}(1 - 0.4b)}{2(1 - b)^2} \,. \tag{32}$$

According to the above equation, the renormalized Madelung constant varies from 0.35 to 0.31 when γ is in the range $(0.5-0.7)R_s$, i.e. is almost three times smaller than that in the one-component plasma model, equal to 0.9. This conclusion is of importance for the equation of state, being confirmed by a more sophisticated analysis of the electronic structure of atomic cells which we make in the next section.

6. Model of ellipsoidal cells

In this section we consider a model of ellipsoidal Wigner– Seitz cells adapted for the percolation structure. In general, a virtual atom is a part of the quasi-molecules formed by neighboring atoms in the percolation cluster. However, in the atomic cell model the average interaction between neighboring atoms is described by a cell potential with a smoothed angular dependence. With an infinite number of neighboring atoms, the cell potential can be presented (in 4 dimensions) as an envelope of self-consistent potentials on the axis of the quasi-molecules. The potentials are created by two remainder ions and by the electron cloud which gives a rather weak coordinate dependence, particularly near the symmetry center of the quasi-molecule. To simplify the problem radically, we consider the electron cloud potential outside the ion core as constant [14].

In disordered systems, atomic cells are Voronoi polyhedra which are close to the Wigner–Seitz cells approximated by spheres in closely packed structures. In a looser percolation structure, atomic cells are approximated by ellipsoids circumscribing the classically accessible spheres. By construction, the surface of atomic cells consists of symmetry planes of diatomic quasi-molecules formed by a central atom in the cell and its neighbors. Analogously, the surface of the ellipsoidal cell can be considered the locus of the symmetry centers in such quasi-molecules.

With a definite excitation energy, the radius of the classically accessible sphere is given by

$$R_{\rm a}(\varepsilon_p) = \frac{R_{\rm a}}{1 - \varepsilon_p / I} \,. \tag{33}$$

The cells can be considered identical only in the case when neighboring atoms have the same excitation energy. However, in the following the solution can be renormalized, thus removing this limitation. In the system of excited virtual atoms, the classically accessible volume fraction is

$$\zeta(\varepsilon_p) = \frac{\zeta_0}{\left(1 - \varepsilon_p / I\right)^3} \,. \tag{34}$$

The simplest form of the cell nearest to the sphere is an oblate ellipsoid (Fig. 4):

$$R(\vartheta) = \frac{R_{a}(\varepsilon_{p})}{\sqrt{1 - [1 - \zeta(\varepsilon_{p})/f]\sin^{2}\vartheta}},$$
(35)

where $R(\vartheta)$ is the radius, ϑ is the polar angle, and $f \approx 2/3$ is the random close packing factor of the spheres. At the poles, the inscribed classically accessible sphere touches those of neighboring atoms. The polar half-axis of the ellipsoid is equal to the classically accessible radius $R_a(\varepsilon_p)$, and the volume is the fraction f of the Wigner–Seitz cell volume. In the case $\zeta(\varepsilon_p) = f$, the cell coincides with the classically accessible sphere. Thus, due to the excitation of virtual atoms the ellipsoidal cells are rounded, approaching the sphere. Physically, the rounding of the cells is connected with an atomic displacement which is slow compared to electronic processes.



Figure 4. Ellipsoidal atomic cell circumscribing the classically accessible sphere of the valence electron in a virtual atom [15].

We consider a one-electron problem with the effective cell potential

$$V(r,\vartheta) = v \big[R(\vartheta) + \rho \big] + v \big[R(\vartheta) - \rho \big], \qquad (36)$$

where $\rho = r - R(\vartheta)$, *r* is the radial coordinate, and v(r) is the Heine–Abarenkov-like pseudopotential:

$$v(r) = \begin{cases} -\frac{e^2}{r_{\rm c}}, & r < r_{\rm c}, \\ -\frac{e^2}{r} + \frac{\xi I}{2}, & r > r_{\rm c}, \end{cases}$$
(37)

where r_c is the effective radius of the ionic core. Outside the ionic core, the Coulomb potential acquires an additive constant which is half the electron cloud potential. The core radius is determined by the condition that the ionization potential of a free atom is reproduced at $\xi = 0$.

To determine the unknown parameter ξ , we use a percolation condition implying that the valence electron energy is equal to the potential saddle between the classically accessible spheres touching at the poles of neigh-

boring cells:

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$$E = -2(I - \varepsilon_p) + (\xi + \delta)I.$$
(38)

In Eqn (38), the first term in the right-hand side corresponds to the sum of the Coulomb potentials created by remainder ions of the quasi-molecule. In the second term, the ξ item relates to the electron cloud potential, and the δ item stands for the centrifugal potential caused by an admixture of higher angular momenta to the *s*-wave ground atomic state in the absence of spherical symmetry.

The pseudowave function is determined by the Schrödinger equation

$$\Delta \Psi + \frac{2m}{\hbar^2} \left[E - V(r, \vartheta) \right] \Psi = 0$$
(39)

with the boundary conditions $\partial \Psi / \partial r = 0$ at the origin and on the cell surface. Substituting the percolation condition defined by Eqn (38) into the Schrödinger equation, we obtain an additional boundary condition $\partial^2 \Psi / \partial r^2 = 0$ at the ellipsoid poles, which allows us to determine the unknown factor ξ . The wave function is expanded in terms of the eigenfunctions of the angular momentum:

$$\Psi = \sum_{l=0,2,\dots} a_l \Phi_l(r) Y_{l0}(\cos \vartheta) , \qquad (40)$$

where $Y_{l0}(\cos \vartheta)$ are the spherical functions with the projection of the angular momentum m = 0, $\Phi_l(r)$ are normalized radial functions, and a_l are coefficients normalized by the condition $a_0 = 1$. Substituting the series expansion (40) into the Schrödinger equation and projecting onto the state of a definite angular momentum l, one obtains a system of coupled ordinary differential equations for the radial functions $\Phi_l(r)$ [15]:

$$\left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr}\right) - \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2} E\right] a_l \Phi_l(r)
= \frac{2m}{\hbar^2} \sum V_{ll'}(r) a_{l'} \Phi_{l'}(r), \quad l = 0, 2, \dots,$$
(41)

where $V_{ll'}(r) = \langle Y_{l0} | V(r, \vartheta) | Y_{l'0} \rangle$ are the matrix elements of the potential. Generally, only a few partial waves considerably contribute to the wave function (40). By numerical integration of Eqns (41) along the polar, equatorial, and corresponding number of intermediate directions with a Newton iteration, one determines the energy *E*, the ξ factor, and the unknown coefficients a_l which satisfy the boundary conditions at the center and on the surface of the cell. A characteristic feature of the pseudowave function Ψ is a plateau near the ellipsoid poles, which occupies almost the whole region outside the ionic core (Fig. 5).

The interaction energy of one atom with all others is determined by the difference between the energy *E* and that of noninteracting virtual atoms, $-I + \varepsilon_p$. Summing over all the atoms, each atomic interaction contributes twice, therefore the interaction energy per atom is

$$u = \frac{1}{2} \left(E + I - \varepsilon_p \right). \tag{42}$$

At definite ζ_0 , the interaction energy is a function of the classically accessible volume of excited electrons and must still be averaged over ζ from ζ_0 to close packing factor *f*.



Figure 5. Pseudowave function along the polar and equatorial radii of the ellipsoidal atomic cell for $\zeta_0/f = 0.8$ (solid line) and $\zeta_0/f = 1.0$ (dotted line) [14].

The result of calculations [15] with $r_c = 0.68 R_a$ which is characteristic of heavy alkali metals has been approximated by a linear function of ζ (Fig. 6):

$$u(\zeta_0, \zeta) = 0.0662 - 0.5183\zeta_0 - b(1.8862 - 1.4867\zeta_0)(\zeta - \zeta_0), \qquad (43)$$

where b = 1/2 is the symmetry coefficient of the diatomic quasi-molecules. Provided that the virtual contribution of each quasi-molecule depends on the average volume of the classically accessible spheres of the two constituent atoms, the



Figure 6. Interaction energy as a function of the classically accessible volume of an excited electron [15].

symmetry coefficient allows us to map the linear dependence on ζ , caused by the simultaneous excitation of all the atoms, onto the problem of the excitation of a single atom at the cell center.

Calculation of the mean interaction energy becomes essentially simpler because the excitation energy is almost compensated by energetically advantageous rounding of the cells. Due to compensation, the total excitation energy is much smaller than the critical temperatures of alkali plasmas:

$$\Delta E = \varepsilon_p + u(\zeta_0, \zeta) - u(\zeta_0, \zeta_0) \ll T_c.$$
(44)

Since all rounded cells have practically the same probability of occurrence, the interaction energy is averaged by a simple integration:

$$u(\zeta_0) = \frac{1}{f - \zeta_0} \int_{\zeta_0}^f u(\zeta_0, \zeta) \,\mathrm{d}\zeta \,. \tag{45}$$

As a result of averaging over the rounded cells, the interaction energy goes independent of the details of their electronic structure and turns out to be rather close to the Madelung energy with the constant $\gamma = 0.32-0.34$ (Fig.7). Thus, the cell model confirms the estimate of the Madelung constant discussed in the previous section for the quasiclassical case typical of heavy alkali metals with great ionic core radii.

In lithium, the relative radius of the ionic core $r_c = 0.6R_a$, being considerably smaller than in heavy alkali metals, results in a numerical deviation of the Madelung constant. By solving the problem for spherical cells in random close packing ($\zeta_0 \approx 2/3$) we find that the percolation condition



Figure 7. Mean interaction energy versus volume fraction of classically accessible spheres [15]. The dot-and-dash line corresponds to fixed cells, and the solid line to rounded cells. The dashed line is the renormalized Madelung energy.

(38) is satisfied only in the limiting case E = -2I corresponding to the maximum-in-modulus interaction energy u = -I/2. Then it follows that the Madelung constant $\gamma = -u/I\zeta_0^{1/3} \approx 0.55$ is about 1.5 times greater than in caesium. Such a distinction of lithium may be the reason for its deviation from the similarity laws justified for heavy alkali metals (see the next section). Thus in the quasi-classical case, its estimate (32) obtained with a uniform distribution of the electron density is confirmed, but the atomic cell model also shows that the Madelung constant varies in different metals due to quantum effects.

7. Van der Waals equation

In this section we will give direct estimates for the Coulomb critical points of metals using the simplest equation of state of virtual atoms. Similar to charged hard spheres, this equation can be presented as a van der Waals equation of state. However, a distinctive feature of virtual atoms is that valence electrons directly contribute to the pressure by their random walk on atoms with thermal excitation energies. Since in the initial and final states the electron wave packet is centered on the atom, an electron excluded volume coincides with that for atoms as composite particles. Thus taking into account the electron contribution to the pressure, the equation of state is written as

$$p = \frac{(z+1)n_{\rm a}T}{1-4\eta} - \frac{\gamma}{3} \left(\frac{4\pi}{3}\right)^{1/3} z^2 e^2 n_{\rm a}^{4/3} \,, \tag{46}$$

where z is the number of valence electrons of the atom, and η is the packing factor of the hard spheres of diameter $d = e^2/I$:

$$\eta \approx \frac{\pi}{6} \left(\frac{e^2}{I}\right)^3 n_{\rm a} \,. \tag{47}$$

The critical temperature determined by this equation of state [15] with the conditions $\partial p/\partial n = \partial^2 p/\partial n_0^2 = 0$ is

$$T_{\rm c} = \frac{16}{49} \left(\frac{2}{7}\right)^{1/3} \frac{\gamma z^2 I}{z+1} , \qquad (48)$$

the critical pressure

$$p_{\rm c} = \frac{1}{49} \left(\frac{2}{7}\right)^{1/3} \frac{\gamma z^2 I}{2\pi} \left(\frac{I}{e^2}\right)^3,\tag{49}$$

and the critical density

$$n_{\rm ac} = \frac{2}{7} \, \frac{3}{4\pi} \left(\frac{I}{e^2}\right)^3. \tag{50}$$

Thus, the critical parameters turn out to be expressed via the ionization potential and the valence of atoms. From these equations it follows that the critical value of the coupling parameter defined by Eqn (28) equals

$$\Gamma_{\rm c} = \frac{49}{16} \, \frac{z+1}{\gamma} \,. \tag{51}$$

For instance, in alkali plasmas with z = 1 it follows that $\Gamma_c \approx 18$, i.e. the Coulomb condensation occurs in strongly coupled plasmas (note that the Debye-Hückel theory already signals the phase transition when $\Gamma \sim 1$).

When applied to alkali metals, Eqns (48)–(50) with z = 1 give rather good estimates. For example, with $\gamma = 0.33$ the critical temperature of caesium deviates from the experimental value [35] by about 15%, and the critical pressure by 5%. According to these formulas, the critical value of the classically accessible volume fraction is $\zeta_0 = 2/7 \approx 0.286$, which should be compared to that found from the experimental critical density, $\zeta_0 \approx 0.365$ [35]. As can be seen from the data given in Table 1, there is a similar correspondence for other alkali metals as well (the only exception is the critical density of sodium for which the experimental estimate is less accurate). Thus, the simple van der Waals equation correctly describes the main features of the problem. According to Eqns (48)–(50), there is an approximate scaling

$$T_{\rm c} \propto I, \quad p_{\rm c} \propto I^4, \quad n_{\rm ac} \propto I^3,$$
 (52)

which is confirmed by available experimental data.

There is every indication that lithium has a Coulomb critical point but it is expected to deviate from the scaling law (see the end of Section 6). Although the critical point of lithium has not been experimentally determined, the deviation from the similarity laws defined by Eqns (52) is revealed by a bad correspondence of estimated critical parameters with the saturation pressure extrapolated to the critical temperature [36]:

$$p_{\rm s} \propto T^{-m} \exp\left(-\frac{q}{T}\right), \quad m \approx 0.5,$$
 (53)

where q is the heat of evaporation at $T = 0^{3}$. All the estimated critical points of alkali metals are located in the saturation pressure curves given by Eqn (53), while that of lithium turns out to be considerably above it. However, with the limiting value of the Madelung constant γ predicted for lithium, Eqns (48) and (49) give the critical point at a higher temperature (see Table 1) to agree with Eqn (53).

It should be noted that the above-mentioned calculations in the approximation of weak electron—ion coupling give a critical temperature up to five times higher or in the model of partial ionization the critical pressure as many times higher than experimental values (with the exception of lithium, described a bit better) [9]. The numerical calculations based on the tight-binding approximation (taken from the oneelectron theory of solids) combined with the lattice gas model for ions [12, 13] are closer to the experimental data but not as good as estimates made with the van der Waals equation for virtual atoms.

8. Three-parameter equation of state

In this section we will consider the scaling of critical parameters with respect to the ionization potential and valence of ions, which allows us to estimate unknown parameters for a number of metals with normalization to the critical parameters of caesium. The main idea is that the parameters of the van der Waals equation, namely, the hardsphere diameter and the Madelung constant, can be found empirically using available critical data [6]. However, an approximate equation with two parameters does not allow approximation of the critical values of three thermodynamic

³ Since the heat of evaporation is much greater than the critical temperature, the saturation pressure grows exponentially up to the critical point, thus making the extrapolation rather definite.

Metal	<i>T</i> _c , K	$p_{\rm c}$, bar	$\rho_{\rm c},{\rm g~cm^{-3}}$	Method	Reference
Cs (6s)	1600	87	0.3	Van der Waals equation for virtual atoms	[15]
	2000	460	0.55	Partially ionized gas	[9]
	2350	60	0.47	Lattice gas & tight-binding approximation	[12]
	1924	92.5	0.38	Experiment	[35]
Rb (5s)	1720	115	0.24	Van der Waals equation for virtual atoms	[15]
	2200	650	0.45	Partially ionized gas	[9]
	2475	73	0.35	Lattice gas & tight-binding approximation	[12]
	2060	123	0.3	Scaling normalized to caesium	[37]
	2017	124	0.29	Experiment	[35]
K (4s)	1790	134	0.12	Van der Waals equation for virtual atoms	[15]
	2350	690	0.21	Partially ionized gas	[9]
	2550	70	0.22	Lattice gas & tight-binding approximation	[12]
	2140	144	0.16	Scaling normalized to caesium	[37]
	2178	150	0.17	Experiment	[75]
Na (3s)	2115	263	0.12	Van der Waals equation for virtual atoms	[15]
	2400	1400	0.27	Partially ionized gas	[9]
	2970	128	0.22	Lattice gas & tight-binding approximation	[12]
	2535	282	0.15	Scaling normalized to caesium	[37]
	2485	248	0.30	Experiment	[75]
Li (2s)	3700	530	0.042	Van der Waals equation for virtual atoms	This work
	3500	770	0.025	Partially ionized gas	[9]
	2660	342	0.053	Scaling normalized to caesium	[37]
	3225	690	0.1	Extrapolation	[40]
Cu (4s ²)	7620	5770	1.4	Scaling normalized to caesium	[37]
	8390	7460	2.4	Extrapolation	[40]
Al (3s ² 3p)	8860	4680	0.28	Scaling normalized to caesium	[37]
	8000	4470	0.64	Extrapolation	[40]
Be (2s ²)	9200	12200	0.35	Scaling normalized to caesium	[37]
	8100	11700	0.55	Extrapolation	[40]
U (7s ² 7p)	9000	5000	2.6	Scaling normalized to caesium	[45]
	11600	6100	5.3	Extrapolation	[40]
La (6s ² 6p)	8250	3500	1.2	Scaling normalized to caesium	[45]
	11000	3350	1.8	Extrapolation	[40]
Y (5s ² 5p)	9500	6000	1.1	Scaling normalized to caesium	[45]
	10800	3700	1.3	Extrapolation	[40]

Table 1. Ci	ritical parame	eters of me	tallic fluids
	ritietti pterterine	veero or me	course montaio

variables. This becomes obvious when expressing the critical compressibility factor from Eqns (48) - (50):

$$Z_{\rm c} = \frac{p_{\rm c}}{n_{\rm a\,c}T_{\rm c}} = \frac{7}{48} \left(z+1\right). \tag{54}$$

For alkali metals (z = 1), the magnitude of this factor is about 0.29 that is due to adding errors 45% greater than the experimental value 0.2 [35]. In contrast to the van der Waals equation, an equation of state with three parameters [37] allows us to approximate the critical values of three thermodynamic variables and thus to compare theoretical estimates of both the hard-sphere diameter and the Madelung constant with the experiment.

For a finite packing factor of hard spheres, the range of applicability of the equation of state extends a little by substituting the Carnahan–Starling function [Eqn (17)] for the van der Waals function of excluded volume:

$$p_T = (z+1)n_a TF(\eta)$$
. (55)

Since the cell model with smoothed angular dependence of the potential corresponds to the limit of great coordination numbers $N_c \sim (2R_a/R_s)^3 \ge 1$, the Madelung energy can be considered the first term of a power expansion in a small parameter:

$$U = -\gamma n_{\rm a} \frac{z^2 e^2}{R_s} \left[1 + \beta \frac{R_s}{2R_{\rm a}} + \delta \left(\frac{R_s}{2R_{\rm a}} \right)^2 + \dots \right].$$
(56)

Restricting the expansion to three terms and requiring that the energy as a function of R_a is maximum in modulus when $R_a = R_s$, we obtain $\beta > 0$ and $\delta = -\beta < 0$. Correspondingly, an expansion for the pressure is the following

$$\Delta p = -\frac{\gamma z^2 e^2 n_{\rm a}}{3R_s} \left(1 + \beta \frac{R_s^2}{4R_a^2}\right),\tag{57}$$

where the coefficient δ is expressed by β . The second term in Eqn (56) does not contribute to the pressure, since the factor

 R_s which contains the volume dependence reduces. Collecting terms, we obtain

$$p = n_{\rm a} \left[(z+1) T F(\eta) - A \eta^{1/3} - B \eta^{-1/3} \right], \tag{58}$$

where

3.0

$$A = \frac{\gamma z^2 I}{3c}, \quad B = \frac{\gamma \beta c z^2 I}{12}, \quad c = \frac{d}{2R_a}$$

and *d* is the hard-sphere diameter. The parameters in Eqn (58), determined by the caesium critical data involving the compressibility factor $Z_c = 0.2$, the volume fraction of the classically accessible spheres $\zeta_c = 0.365$, and the temperature $T_c/I = 0.0425$, are c = 0.47, $\gamma = 0.34$, and $\beta = 0.23$ [37]. Thus, the hard-sphere diameter is approximately equal to the radius of the electron shells, and the Madelung constant practically coincides with that found from the model of ellipsoidal cells. The small values of the coefficients β and δ show that expansion (56) has a meaning.

With the relative pressure $\pi = p/p_c$, density $v = n_a/n_{ac}$, and temperature $\tau = T/T_c$, equation (58) becomes

$$\pi = 10v \left[\tau F(\eta) - A_0 \eta^{1/3} - B_0 \eta^{-1/3} \right],$$
(59)

where $A_0 = 2.854$, and $B_0 = 0.03643$. Due to the high critical expansion, the coexistence curve determined by this equation is considerably more asymmetric than in neutral fluids (Fig. 8). It is interesting that at the relative densities v = 0.5 - 1.5 near the critical point, the boiling and condensation lines agree well with the experiment. However, the range of applicability of the mean field theory is still vague because even in a greater density range the coexistence curve and the mean diameter are approximated by scaling dependences with universal critical indices as well [35].



Figure 8. Density – temperature phase diagram in the vicinity of the critical point of metallic fluids [37]. The experimental dots for caesium (circles) and rubidium (stars) are from Jüngst et al. [35].

The critical parameters determined by Eqn (58) are expressed by the same functions of the ionization potential and the valence as for the van der Waals equation, but with numerical coefficients normalized to the critical point of caesium:

$$T_{\rm c} \approx 0.085 \frac{z^2 I}{z+1} \,,$$
 (60)

$$p_{\rm c} \approx 0.405 z^2 I^4 \,, \tag{61}$$

$$n_{\rm ac} \approx 2.92 \times 10^{19} I^3 \,,$$
 (62)

$$Z_{\rm c} = 0.1(z+1)\,,\tag{63}$$

where *T* and *I* are measured in eV, p_c in bars, and n_{ac} in cm⁻³. Equations (60)–(62) are somewhat more accurate than the analogous formulas (48)–(50). However, similarity between metals occurs only for the same relative hard-sphere radii *c*, and the same coefficients γ and β , i.e. can be only approximate. Nevertheless, the similarity laws allow us to estimate the critical parameters promptly in the absence of detailed calculations for specific metals.

Except for the dependence of the critical temperature on the valence, which reduces to their proportionality only in the case of great valence $z \ge 1$, the other functions of *I* and *z* in Eqns (60)–(62) are governed by power laws corresponding to the absence of characteristic values. Within the limits of uncertainty, the formula for the temperature can also be presented by a power law

$$T_{\rm c} \approx 0.0425 z I. \tag{64}$$

The power laws ruled by Eqns (61), (62) and (64) yield a scaling of the Coulomb critical points of metals with respect to the ionization potential and the valence of atoms. A relationship between the critical pressure and temperature for arbitrary valence also follows from Eqns (61) and (64):

$$p_{\rm c} \approx 225 I^2 T_{\rm c}^2 \,. \tag{65}$$

As can be seen from Table 1, the measured critical points of heavy alkali metals are well described by scaling (except the critical density of sodium, which is worse known). However, lithium deviates from the similarity, thus indicating that one should be careful with scaling. Additional information for more definite estimates can be given, for example, by the relationship between the temperature and pressure extrapolated along the vapor pressure curve. In many cases [38], Eqns (61) and (64) reasonably agree with the thermodynamic estimates of critical temperatures and pressures [39, 40], which are based on available characteristics of condensed phases and some other data (see examples in Table 1).

9. Metal-ammonia solutions

Solutions of metals, such as Na, in liquid ammonia [41] give a unique possibility to observe a phase transition with a Coulomb critical point easily available in the laboratory conditions. As was noticed long ago, the solution layering into dilute (polaronic) and concentrated metal-rich phases below the consolute temperature of 230 K is analogous to the condensation of a dissolved metal. It was believed that the consolute point is determined by the Coulomb interaction [42], since the polaronic phase is an electrolyte, and the metal-rich phase is a metal. Moreover, at the consolute point the conductivity reaches a minimum metallic value $\sim 10^2 \,\Omega^{-1} \,\mathrm{cm}^{-1}$ [43], the atomic number density of dissolved metal being of the same order as at the critical points of condensation in pure alkali metals.

Metal-rich solutions differ from those diluted by strong electron – ion coupling which results in overlapping impurity states of alkali atoms in liquid ammonia. Analogously to pure alkali metals, near the consolute point the phase transition is caused by interaction of overlapping impurity atoms. However, the characteristics of impurity states and interactions between them are strongly influenced by liquid ammonia as a nonlinear dielectric medium with a strong frequency dispersion.

At high frequencies, the permittivity of liquid ammonia, caused by electronic polarization of molecules, is $\varepsilon_{\infty} \approx 2$. High permittivity at low frequencies ($\varepsilon_0 \approx 22$) is mainly caused by the orientation of permanent dipoles of ammonia molecules. By virtue of the inertia of molecules, an electron creates a polaron potential well with Coulomb asymptotics $-(\varepsilon_{\infty}^{-1} - \varepsilon_{0}^{-1})e^{2}/r$ (outside the main region of localization) [44]. The impurity state has a potential obtained by summing the polaronic and ionic potentials, i.e.

$$v = -\frac{e^2}{\varepsilon_{\infty} r} \,, \tag{66}$$

and the classically accessible radius

$$R_{\rm a} = \frac{e^2}{\varepsilon_{\infty} I} \,, \tag{67}$$

where *I* is the impurity ionization potential. Due to a great static permittivity, the impurity potential differs from the polaronic potential rather little. Therefore, the classically accessible radius can be estimated from Eqn (67) with the polaronic binding energy $I \approx 1.6$ eV found from the optical absorption spectra of dilute solutions. Analogously to alkali plasmas, impurity atoms form percolation clusters of overlapping classically accessible spheres of radius R_a defined by Eqn (67), the interatomic repulsion being modelled by hard spheres of such a diameter $d = R_a$.

The interaction between overlapping impurity atoms, determined by the main region of electron localization, thus decreases by virtue of the high static permittivity. However, at the mean ammonia intermolecular distance the dipole polarization in the ion field is saturated, therefore the permittivity differs from the macroscopic value. The polarization vector of dipole molecules in the ion field is given by

$$P = \frac{\varepsilon_{\rm eff}(r) - \varepsilon_{\infty}}{4\pi} \; \frac{e}{\varepsilon_{\rm eff}(r)r^2} \;, \tag{68}$$

where $\varepsilon_{\text{eff}}(r)$ is an effective permittivity which depends on the distance from the ion due to the saturation of polarization. Equating this expression to a saturated polarization P = dN, where *d* is the dipole moment, and *N* is the molecular number density in liquid ammonia, we obtain the upper limit of permittivity

$$\varepsilon_{\text{eff}}(r) < \frac{\varepsilon_{\infty}}{1 - r^2/R_d^2}, \quad R_0 < r < R_d \left(1 - \frac{\varepsilon_{\infty}}{\varepsilon_0}\right)^{1/2},$$
 (69)

where $R_0 = (4\pi N/3)^{-1/3}$ is the molecular cell radius, and $R_d = \sqrt{e/4\pi dN}$ is the saturation radius of polarization. To average over the Wigner–Seitz impurity cell, we use an integral expression for the potential:

$$\frac{1}{\varepsilon_{\rm eff}} = \left(\frac{1}{R_0} - \frac{1}{R_s}\right)^{-1} \int_{R_0}^{R_s} \frac{\mathrm{d}r}{\varepsilon_{\rm eff}(r)r^2} \,,\tag{70}$$

with ε_{eff} defined by Eqn (69) in the range of saturation or by $\varepsilon(r) = \varepsilon_0$ beyond this range. At the consolute point we obtain $\varepsilon_{\text{eff}} < 9$, i.e. the average effective permittivity is 2.5–3 times smaller than the macroscopic value.

On the other hand, the impurity ionization potential and the effective permittivity can be estimated semiempirically via the experimental temperature and concentration at the consolute point of sodium–ammonia solutions. We use formulas (47)–(49) for the solution replacing *I* with $\varepsilon_{\infty} I$ and γ with $\gamma/\varepsilon_{\text{eff}}$. Normalizing to the critical point of caesium, we have

$$n_{\rm ac} = 2.92 \times 10^{19} (\varepsilon_{\infty} I)^3 ,$$
 (71)

$$T_{\rm c} = 0.0425 \frac{\varepsilon_{\infty}}{\varepsilon_{\rm eff}} I.$$
⁽⁷²⁾

Substituting in these equations the density of sodium corresponding to the critical concentration 4.15% as well as the number density of molecules 2.55×10^{22} cm⁻³ and the critical temperature $T_c = 230$ K [43], we find $I \approx 1.65$ eV and $\varepsilon_{eff} \approx 7$ in agreement with the estimates above. Thus, the parameters of the consolute point contain information on the impurity states of metal atoms and nonlinear dielectric properties of liquid ammonia.

10. Critical valence of the transition metals

The majority of elements in the Periodic Table are metals, most of them being transition metals with partially filled dand f-shells. Close to the metal-insulator transition, the valence (ion charge number) of these metals is different from that at normal density. The main point here is that the radii of d- and, especially, f-shells are considerably smaller than the radii of valence s-shells [28]. In condensed metals, d-electrons are generally related to the valence electrons, but near the percolation threshold of s-shells they are considered internal, since d-shells are still far from overlapping. Thus, the question of ionic valence at the critical point reduces to the possibility that internal electrons are excited into the outer spshells.

Due to the many-particle exchange interaction between virtual atoms, the electron excitation changing the valence electron configuration of virtual atoms can be energetically advantageous and strongly influences the critical temperature and pressure. This effect is analogous to changing the electron configuration of transition metal atoms forming molecules (but d-electrons can also directly participate in chemical bonding thus increasing the maximum chemical valence up to 6 [28]). The total excitation energy depends on the relation between that of the electron configuration with higher ionic valence and the corresponding change of the exchange interaction energy.

For the ground electron configuration $(n-1) d^k ns^2$ with a great principal quantum number *n*, the excitation energy of another configuration $(n-1) d^{k-1} ns^2 np$ can be estimated in a crude approximation with a semiclassical model. By semiempirical rules, a d-electron has nearly the same energy, and a p-electron nearly the same characteristic radius as an s-electron. With this rule, the excitation energy of the displaced term is equal to the centrifugal energy of the p-electron at the characteristic radius R_a :

$$\Delta E = \frac{l(l+1)\hbar^2}{2mR_a^2} = \frac{I^2}{2Ry} \,. \tag{73}$$

Formula (73) correlates with the excitation energies of known displaced terms (Fig. 9) and can be used for crude estimates in the absence of experimental data. According to this formula, the excitation energy of the displaced term of uranium, for example, is close to that known for thorium, and the displaced term of tungsten is close to that of tantalum.



Figure 9. Excitation energy of the displaced terms in atoms of transition metals. Squares are experimental terms taken from Radzig et al. [30], and circles correspond to those estimated for uranium and tungsten. The solid line is calculated from Eqn (73).

At the critical point, the total energy of the transition into such a displaced term includes the change of interatomic interaction due to increasing ionic valence:

$$\Delta E_{\rm c} = \frac{I^2}{2\rm Ry} - \gamma (z_{\rm c}^2 - z^2) I \zeta_0^{1/3} , \qquad (74)$$

where z = 2 is the ionic valence in the ground electron configuration of the atom, and $z_c = 3$ is the effective valence corresponding to the displaced term. Substituting $\gamma = 0.33$ and the critical value of the classically accessible volume, $\zeta_0 = 0.365$, it can be verified that for every possible ionization potentials the total excitation energy ΔE_c is negative, and in order of magnitude is equal to -I.

Thus, the excitation of displaced terms is energetically advantageous. In most cases, transition metals have the electron configuration $(n-1) d^k ns^2$, therefore the critical ionic valence is increased to 3. An increase of the valence z

by 1 can still be considered a small perturbation of the order of $1/z_c \sim 1/3$, but many-electron transitions increasing the valence even more are apparently beyond the concept of virtual atoms which differ little from free atoms.

In consequence of increasing ionic valence, the critical compressibility factor of transition metals becomes equal to $Z_c = 0.1(z_c + 1) = 0.4$, i.e. two times greater than in alkali metals. Generally, critical temperatures and pressures of transition metals estimated by scaling laws due to Eqns (61), (62) and (64) with the critical ionic valence $z_c = 3$ [45], correlate quite well with available semiempirical estimates (Table 1).

11. Percolation transition in liquids

The problem of existence of the Coulomb critical points is inseparable from the more general problem of the insulator metal transition. The nature of the critical point essentially depends on its position in the phase diagram with respect to this transition. Besides, the insulator-metal transitions are of interest in a wider class of fluid systems than liquid metals having Coulomb critical points, for instance, in inert gases, hydrogen, other semiconducting and dielectric fluids and disordered solids as well. In fluids and disordered solids, the insulator - metal transition is drastically different from that in crystalline solids determined by the electronic band structure. In various liquids such transitions have their own features, by no means described with generally used theoretical models. At the same time, there is also something common to all the insulator-metal transitions in liquids. In particular, the surprisingly easy metallization of liquid hydrogen as compared to solid [46] is in fact typical and has even been predicted by analogy with liquid iodine [47]. In this section, we will consider examples of insulator-metal transitions in different systems and the Coulomb interaction effects related to the insulator-metal transition from recent works.

11.1 Role of structure

In semiconducting and dielectric liquids, the insulator – metal transition resides certainly above the critical density. Therefore, the critical point corresponds to equilibrium between two dielectric phases and is determined by the van der Waals rather than the Coulomb interaction. One such liquid is mercury which is semiconducting when expanded more than one and a half times, although it is metallic at normal density. An alternative example is selenium, a semiconductor with an energy gap of 2 eV, which becomes metallic in melt at elevated temperature and a pressure of the order of 10 kbar.

The insulator – metal transition depends on the density as well as on the atomic structure of condensed matter. It is well known that germanium and silicon, crystalline and amorphous semiconductors, become metals in melts [42]. Boron, an insulator in crystalline state, becomes a metal being melted, despite a little decrease in the density [48]. Selenium [49] and iodine [47] transfer into a metallic state when they are melted under a pressure higher than about 35 kbar. Liquid hydrogen is metallized being compressed ninefold [46], though the solid remains dielectric at the maximum reached compression. Evidently, it is easier to make the transition into the metallic state in liquids than in solids due to lesser importance of quantum diffraction. In the absence of quantum interference and Anderson localization [50], percolation of overlapping electron shells becomes the condition of metallization brought to forefront.

11.2 Mercury

The metal – insulator transition in expanded liquid mercury at about the critical temperature is the best studied [2]. The transition density is experimentally determined by the disappearance of the activation energy extrapolated from the insulator side or by the Knight shift on the metal side, the results being consistent with each other. In contrast, attempts to relate the insulator – metal transition to closing of the optical gap led to misunderstanding (see, for example, book [53] and references cited therein), because the transparency window in optical spectra vanishes due to a polarization shift of the resonance atomic energy level in fluctuation clusters [51, 52].

The insulator-metal transition point, $\rho_{IM} \approx 9 \text{ g cm}^{-3}$, corresponds to the classically accessible volume fraction $\zeta_0 = 0.3$ equal within a few percent to the minimum percolation threshold of overlapping shells with hard cores (see Fig. 3). In this density range, the hard-core diameter found in the Carnahan-Starling approximation by fitting the p-V-Tdata of a saturated liquid goes through a weak minimum, $\sim 2.4 \text{ Å}$ [2]. The ratio of the hard-core diameter to the shell diameter is about 0.8, i.e. approximately corresponds to the minimum of the shell percolation threshold (Fig. 3).

The structure of expanded liquid mercury studied by Xray diffraction shows a first peak of the radial distribution function located at about 3 Å [54], i.e. within 10% of the electron shell diameter. At the density 9 g cm⁻³, the average number of neighboring atoms in the first peak (i.e. the coordination number of liquid) varies from 4 to 6 according to different experimental estimates, and about half the atoms are located in a percolation sphere of radius $2R_a$. The estimate suggests proximity to the percolation threshold, although in this way it is rather difficult to determine the number of overlapping atoms more accurately.

The p-V-T data [2, 55] and the sound velocity [56] do not show any thermodynamic peculiarity at the insulator – metal transition point. Evidently, a plasma phase transition (secondary condensation) which otherwise could be caused by the Coulomb interaction is forbidden due to the small compressibility of the liquid. An important conclusion that the insulator – metal transition is continuous can be applied to the whole problem of such transitions in liquids, although it is often ignored. Besides, Kozhevnikov et al. [56] reported on a first-order 'cluster' phase transition near the critical density (~ 6 g cm⁻³). But this statement has been repudiated [57], since the observed phenomena are explained by prewetting (i.e. growth of a liquid film on the surface, see also Hensel and Yao [58]).

Electronic properties such as conductivity, the Hall coefficient and the thermo-emf in the vicinity of the metal– insulator transition are well described by a percolation theory of thermally activated hopping on virtual atoms [33]. When passing through the transition point, all the electronic properties vary continuously. Below the transition point the conductivity is finite due to thermal excitations, but it strongly reduces with decreasing density. A rather sharp decrease of the conductivity is caused by the great ratio of the ionization potential to the temperature, I/T_c , which reaches about 70. If such a parameter goes to infinity, the metal–insulator transition becomes quite sharp, as is observed in impurity semiconductors (see the next section).

11.3 Phosphorus in silicon

Substituting for atoms of silicon in the crystalline lattice, phosphorus atoms form impurity states with a low ionization potential $I_a = 45.5 \text{ meV}$ [23]. The classically accessible radius of impurity states,

$$R_{\rm a}=\frac{e^2}{\varepsilon I_{\rm a}}\,,$$

with $\varepsilon \approx 11.5$ the dielectric constant of the silicon matrix, is considerably greater than the lattice constant of silicon. Therefore, the disordered impurity system is similar to liquids with the percolation threshold of the classically accessible spheres equal to that of the ideal system, $\zeta_0 \approx 0.34$. Indeed, the corresponding phosphorus density $n_a \approx 3.8 \times 10^{18} \text{ cm}^{-3}$ practically coincides with the insulator-metal transition point found experimentally [59].

At a low temperature of the order of 1 mK, the ratio of impurity ionization potential to temperature, I/T, reaches 5×10^5 . Due to the great parameter, the conductivity practically disappears below the transition point, being of metallic character a little above (Fig. 10) [60]. In contrast, at room temperature it is already impossible to differ between activated and metallic conductivities [61]. This example clearly illustrates that the qualitative difference in electronic structure between metal and insulator can be completely masked at high temperatures.

Phosphorus-doped silicon Si:P is a classical disordered system used to study the insulator – metal transition at very low temperatures. An advantage of this system as compared to liquids arises because the Coulomb condensation of impurity atoms fixed in the silicon lattice is forbidden.



Figure 10. Conductivity of doped semiconductors Si:P in the vicinity of the insulator – metal transition versus the phosphorus density at different temperatures [60]. The experimental dots at 0 K (solid squares) are from Rosenbaum et al. [59], and those at 4.2 K (open triangles), 77 K (open squares), and 300 K (open circles) from Yamanouchi et al. [61].

11.4 Selenium

The complex molecular structure of selenium, which may change depending on the temperature and pressure, adds unique characteristics to the insulator-metal transition. Selenium melts into a polymer semiconducting liquid with chain molecules which contain up to 10^5 atoms, gradually dissociating with increasing temperature. The pressure decreases along the insulator-metal transition line from 35 kbar near the melting curve to ~ 1 kbar at the critical temperature (Fig. 11). Near the melting curve, the insulatormetal transition seems to accompany a smeared out phase transition indicated by a 3% decrease of the volume over a small temperature range $\Delta T \sim 50$ K [49]. The phase transition line is described by the Clapeyron-Clausius equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{q}{T(v_2 - v_1)}$$

where q is the transition heat, and v_1 and v_2 are the specific volumes of the semiconducting and metallic phases, correspondingly. If we interpret the phase transition as melting of macromolecules, the negative slope of the transition line in the pressure–temperature plane can be explained by the fragments of melted polymer molecules being packed closer, thus decreasing the volume of liquid. The transition heat estimated by the Clapeyron–Clausius equation, $q \approx 45$ J g⁻¹, coincides in order of magnitude with the ordinary latent heat, supporting the idea of a two-step melting of selenium. Thus, the transition into a metallic state observed in liquid selenium in the range 10–35 kbar is probably a consequence of melting of macromolecules in the polymer melt, similar to that above 35 kbar caused by melting of the solid.

It seems likely that the liquid formed after the melting of macromolecules consists mainly of strongly coupled dimers Se₂. Indeed, at the critical point ($T_c = 1888$ K, $p_c = 385$ bar, $\rho_c = 1.85$ g cm⁻³ [62]) an estimate based on an average value of the critical compressibility factor for the dielectric liquids,



Figure 11. Phase diagram of selenium. Transition lines are: TL, from Brazhkin et al. [49] identified with the melting of macromolecules, and LF, the insulator – metal transition in molecular fluid [64–66].

 $Z_{\rm c} = 0.3$, shows that molecules contain on the average 2.7 atoms. On the other hand, according to the nuclear magnetic resonance data [63], the fraction of end atoms in molecular chains at the critical point, equal to 1/5, corresponds to chains of ten atoms. However, this value characterizes the chain structure of the liquid rather than the constituent molecules.

At the critical temperature, the insulator-metal transition is caused by compression as in expanded fluid mercury. A minimum metallic conductivity $\sim 10^2 \ \Omega^{-1} \ cm^{-1}$ occurs at a density of about 3.2 g cm⁻³ [64, 65], i.e. considerably below the normal density of semiconducting amorphous selenium, $\rho_n = 4.2 \ g \ cm^{-3}$. The conductivity shows a complex temperature dependence which differs from a simple exponential, thus making the activation energy analysis difficult. In such a case, a minimum metallic conductivity remains the main evidence of the insulator-metal transition [66]. As was discussed above for mercury, attempts to determine the transition point by the gap in the optical spectra, already closed at the critical point [67], can only lead to misunderstanding.

Since in the Se₂ molecule the atomic shells do not overlap very strongly, some two thirds of the classically accessible radius, the atoms in the molecules can be considered elements of the percolation cluster. On the other hand, the existing molecular structure obviously influences the percolation threshold of atomic shells. Indeed, the transition point 3.2 g cm⁻³ corresponds to the threshold classically accessible volume fraction $\zeta_{pc} = 0.42$ which considerably exceeds the ideal threshold value. At the transition point, the estimate based on the atomic percolation model gives a conductivity of about 200 Ω^{-1} cm⁻¹, which is consistent with the experimental value.

11.5 Xenon

Dielectric liquids having a wide energy gap are metallized by multiple compression increasing the shell percolation threshold up to a random close packing. Another peculiarity is a steeper self-consistent potential of many-electron shells which goes lower the Coulombic one at the classically accessible radius (Fig. 12). In the quasi-classical case, the difference of these potentials can be estimated by the electron affinity of an isoelectronic negative ion⁴. A negative ion isoelectronic to xenon, I⁻, has the binding energy $\varepsilon_a \approx 3$ eV comparable to the ionization potential of xenon $I \approx 12$ eV. Therefore, the Coulomb part is about 3/4 of the ionization potential. The classically accessible radius is $R_{\rm a} = e^2/(I - \varepsilon_{\rm a})$. Calculating the volume fraction of the classically accessible spheres at the density of liquid xenon, $\zeta_0 \approx 0.27$, we find that the random close packing factor will be already reached for 2.4 times compression. In fact, it was realized in shock waves [68], when the insulator-metal transition is masked by high temperatures. In contrast, solid xenon is metallized by 3.6 times compression [69], which is considerably greater compared to the liquid.

11.6 Hydrogen

Liquid hydrogen is metallized in reverberating shock waves providing tenfold compression under a pressure of about 1.5 Mbar at moderate temperatures 2000 – 3000 K [46]. With

⁴ This is elucidated by the example of metallic clusters of radius *R* with the quasi-classical ionization potential $I = W + (3/8)e^2/R$ and electron affinity $\varepsilon = W - (5/8)e^2/R$ expressed by the work function *W*. The difference $I_{\rm C} = I - \varepsilon$ can be considered a Coulomb ionization potential which determines the classically accessible electron radius $R_{\rm a} = e^2/I_{\rm C}$ equal to the cluster radius *R*.



Figure12. Scheme illustrating the increase of the classically accessible radius in many-electron shells due to the deviation from the Coulomb potential.

the dissociation energy of 4.5 eV, hydrogen molecules are not appreciably dissociated in these conditions. In contrast to atomic systems, the insulator – metal transition is caused here by percolation of overlapping electron shells of virtual molecules.

The classically accessible domain of electron motion in a hydrogen molecule (Fig. 13) is close to a prolate ellipsoid with semiaxes of $1.55a_B$ and $1.95a_B$, which bounds almost the same volume as a sphere of the radius $R_m = e^2/I$, where $I \approx 16 \text{ eV}$ is the ionization potential of the molecule for fixed nuclei. With parallel axes of the ellipsoids, the percolation threshold does not differ from that for spheres. In a general way, with the axes of molecules occurring at arbitrary angles to each other, the sphere percolation threshold gives an upper limit. In a strongly compressed system, the threshold is attained at



Figure13. Classically accessible domain of electrons in a hydrogen molecule [70]. The mean sphere of the same volume is also shown. The scales are in the Bohr radii.

random close packing:

$$\frac{4\pi}{3} \left(\frac{e^2}{I}\right)^3 n_{\rm m} \approx 0.64\,,\tag{75}$$

where $n_{\rm m}$ is the number density of molecules. Equation (75) determines the threshold number density $n_{\rm m} \approx 2.1 \times 10^{23} \text{ cm}^{-3}$ corresponding to the mass density of 0.7 g cm⁻³, which is ten times the normal liquid hydrogen density. This estimate is consistent within 10% with the experimental transition-point density obtained by extrapolating the activation energy of conductivity to zero [46].

According to a theoretical model [70], near the dielectric liquid – molecular metal transition point the conductivity is caused by thermally activated overbarrier hops of electrons on virtual molecules with overlapping classically accessible spheres. Although experimental data are still lacking, and the temperature estimated by approximate calculation of shock compression varies with the density, the qualitative behavior of the conductivity as a function of density is evidently within the framework of this model (Fig. 14).

In recent calculations of the equation of state [11], the insulator-metal transition observed in superdense fluid hydrogen is represented by a jump in the degree of ionization, which gives rise to a weak first-order phase transition with vanishing transition heat and a 15% density gap. Although still not excluded, the phase transition has not been observed yet. Therefore, one may look for the reason in the method of calculation. Indeed, the jump may be caused by an imperfect theory of nonideal plasma, describing bound and free electron states in different approximations without mixing bound states with free motion. However, due to a



Figure14. Conductivity of molecular hydrogen near the insulator – metal transition at different temperatures [70]. Experimental dots are from Weir et al. [46]. The estimated transition point for random close packing of the classically accessible spheres is shown by an arrow.

strong screening in overlapping molecular shells, the discrete electron spectrum disappears and the effective ionization potential of molecules vanishes. For this reason, the usual separation of free electrons from bound ones makes no sense, therefore there is no jump of the ionization degree as well as the density gap. Thus with mixing of free and bound states, the weak first-order phase transition evidently turns into a continuous transition.

Summing up this section, we note that the insulator – metal transition in liquids forms a Coulomb system with new electronic and thermodynamic properties, since partially free electrons contribute, for example, to the conductivity and pressure. However, in the liquid phase this transition is not generally connected with any first-order phase transition, except for such special cases as melting of macromolecules in liquid selenium.

12. Critical point of mercury

In this section we consider the nature of mercury behavior near the critical point which is on the dielectric side of the metal-insulator transition. In contrast to dielectric liquids, at the critical point mercury possesses an appreciable conductivity. The critical parameters are $T_c = 1751$ K, $p_c = 1763$ bar, and $\rho_c = 5.8$ g cm⁻³ [55]. In the density range 4–6 g cm⁻³, i.e. below the critical point, mercury shows properties of a gaseous semiconductor. Its conductivity falls much lower than the minimum metallic value, still remaining ten orders of magnitude higher than in an ideal gas, whereas at constant density the conductivity exponentially increases with increasing temperature. The dielectric constant varies with the density from a few units to ten, that is in the range typical for semiconductors.

The main feature of a gaseous semiconductor is that the energy gap cannot be considered as an experimentally determined parameter, since it depends on the density. In a dielectric model [71], the energy gap compared to the ionization potential decreases due to the decreasing Coulomb attraction at distances longer than the percolation radius:

$$\Delta = I - \frac{e^2}{R_{\rm pc}} \left(1 - \frac{1}{\varepsilon} \right), \tag{76}$$

where ε is the dielectric constant, and $R_{\rm pc}$ is the percolation radius. In the case of full screening, $\varepsilon \to \infty$, formula (76) assumes the form of Eqn (25) for the mobility gap below the percolation transition in the system of virtual atoms.

The permittivity can be estimated using the Clausius– Mossotti formula (or its regularized version) taking into account the polarization of atoms and chemical bonds in quasi-molecules [33]:

$$\varepsilon = 1 + \frac{4\pi n_{\rm a} \alpha}{1 - \varkappa} \,, \tag{77}$$

where $\alpha = \alpha_a + B\alpha_b/2$ is the total polarizability per atom, $\alpha_a = z(e^2/I)^3$ is the atomic polarizability, z = 2 is the number of polarizable s-electrons, $\alpha_b = (4/3)(e^2/I)^3$ is the polarizability of the bond in the quasi-molecule, *B* is the average number of atoms in a coordination sphere of radius $2e^2/I$, and $\varkappa = 4\pi n_a \alpha/3$. Setting the magnitude of *B* to half the liquid coordination number, at the critical density we find the permittivity to be 6, and the corresponding energy gap $\Delta \approx 3$ eV, typical for a semiconductor. The critical-point permittivity found by light reflection in early works [72, 73] reaches 10. New data [74], closer to the theoretical estimates above, take into account a semiconducting liquid mercury film of about 100 Å thick, growing on a sapphire surface above the prewetting temperature [58].

With the minimum free path, the electron-hole conductivity is [71]

$$\sigma = \frac{2e^2}{\pi\hbar\lambda} \exp\left(-\frac{\Delta}{2T}\right),\tag{78}$$

where $\lambda = (2\pi\hbar^2/mT)^{1/2}$ is the thermal electron wavelength. We note that the hole mobility is caused by the overbarrier transitions of valence electrons from neighboring atoms to the bare ion, whereas electrons in the conduction band move between neutral atoms. The density dependence which follows from Eqns (76)–(78), and the order of magnitude of conductivity at the critical point, ~ 0.1 Ω^{-1} cm⁻¹, corresponding to a weak ionization, agree with experimental data [75]. The thermoelectrical coefficient

$$\alpha_{\rm T} \approx \frac{k_{\rm B} \Delta}{2eT} (b_{\rm h} - b_{\rm e}) \,, \tag{79}$$

where $k_{\rm B}$ is the Boltzmann constant, $b_{\rm h}$ and $b_{\rm e}$ are the hole and the electron mobilities, becomes zero at the critical point [76]. This suggests the compensation of competing terms in Eqn (79) that confirms the existence of the hole contribution to conductivity.

The semiconducting state of mercury at the critical point manifests itself in the critical parameters quite different from the scaling with respect to the ionization potential and valence characteristic of the Coulomb critical points in metals. Since the critical point of mercury does not fall under the Coulomb class, the critical parameters are determined by the van der Waals interaction of atoms. However, a peculiarity of the semiconducting liquid is the still considerable role played by many-particle interactions. Indeed, the depth of the pairadditive Lennard–Jones potential estimated via the critical temperature, $\varepsilon \approx (0.6-0.8)T_c$ (see, for example, the book [21]), is 1.5-2 times greater than the bond energy of the van der Waals molecules Hg₂, D = 0.06 eV [77], indicating the importance of nonpair atomic interactions.

13. Exciton condensation

Finally, we consider the Coulomb critical points of nonequilibrium phase transitions limited to the relaxation time. An example is the condensation of excitons into a metallic electron-hole liquid in strongly excited semiconductors, predicted by Keldysh [18]. The critical point is determined here by the exchange interaction of overlapping excitons, like atoms in metals or impurity atoms in metal-ammonia solutions. Within this analogy, we introduce a model of virtual excitons which allows for strong electron-hole interaction, in contrast to the model of two liquids (see the book [19] and references cited therein). Similarly to other systems, the critical point of condensation is determined by the exciton binding energy and the dielectric constant of the semiconductor.

We first consider exciton condensation in silicon, which has been widely studied. Silicon is an intrinsic semiconductor with an indirect energy gap of 1.1 eV between the top of the valence band at the Brillouin zone center and the bottom of six equivalent valleys in the conduction band. An external excitation creates free electrons in the conduction band and holes in the valence band, which at low temperature are bound in excitons with a hydrogen-like energy spectrum, namely

$$E_n = -\frac{\mu e^4}{2\hbar^2 \varepsilon^2 n^2} \,,\tag{80}$$

where *n* is the principal quantum number, $\mu = m_{\rm e}m_{\rm h}/(m_{\rm e} + m_{\rm h})$ is the reduced mass, and $m_{\rm e}$ and $m_{\rm h}$ are the electron and hole effective masses, respectively. In the ground state, the electron and hole being at opposite ends of the diameter from the common center of mass are mainly localized within concentric classically accessible spheres with radii

$$R_i = \frac{e^2}{\varepsilon I_x} \frac{\mu}{m_i} = 2\varepsilon a_{\rm B} \frac{m}{m_i}, \quad i = e, h, \qquad (81)$$

where $I_x = -E_1$ is the exciton binding energy, $a_{\rm B} = \hbar^2/me^2$ is the Bohr radius, and m is the free-electron mass. With its large dielectric constant, silicon plays the role of a continuous dielectric medium, since the classically accessible radii of electrons and holes are much greater than the lattice constant. Ellipsoidal valleys in the conduction band have different longitudinal m_1 and transverse m_t masses. Generally, to simplify the problem the valleys are considered spherical with the effective mass describing the density of states, $m_{\rm e} = m_{\rm l}^{1/3} m_{\rm t}^{2/3} = 0.32m$ [78]. Near the center of the Brillouin zone, the valence band splits into bands of heavy and light holes. The heavy holes with a greater effective mass $m_{\rm h} = 0.52m$ have the lowest excitation energy, thus being the most important. In the ground exciton state the electron forms a shell around the heavy hole, since the ratio of the electron classically accessible radius to that of the holes is 5:3.

In what follows we restrict the full problem to the limiting case of infinitely heavy holes $(m_h \ge m_e)$ with hopping excitons reduced to metastable atoms with the ionization potential

$$I_{\rm a} = \frac{m_{\rm e}}{\mu} I_x = \frac{m_{\rm e}}{m} \frac{\rm Ry}{\epsilon^2}$$
(82)

and the classically accessible radius $R_a = R_e$.

At low density, the system is an excitonic insulator. However, when overlapping electron shells form an infinite percolation cluster, the electrons become partially free due to collective screening. With the radius of shells R_e determined by Eqn (81), the percolation condition is

$$\frac{4\pi}{3} \left(2\varepsilon a_{\rm B} \frac{m}{m_{\rm e}} \right)^3 n_x \approx \frac{1}{3} , \qquad (83)$$

and the threshold density of excitons $n_x \approx 10^{18} \text{ cm}^{-3}$.

In the limit of infinitely heavy holes, the interaction between excitons reduces to that of overlapping virtual atoms. Analogously to normal atomic systems (see Section 4), the repulsion between excitons at small distances can be modelled by hard spheres of diameter $d = R_a$. In the mean field approximation, the attraction is described by a Madelung energy

$$U = -\frac{\gamma e^2}{\varepsilon R_{sx}} , \qquad (84)$$

where $R_{sx} = (4\pi n_x/3)^{-1/3}$ is the exciton Wigner – Seitz radius, and γ is the renormalized Madelung constant. In the case of a small ion core (see the end of Section 6), an appropriate value of the Madelung constant is $\gamma \approx 0.55$.

The equation of state of virtual excitons is written as

$$p = \frac{2n_x T}{1 - 4\eta} - \frac{\gamma}{3} \left(\frac{4\pi}{3}\right)^{1/3} \frac{e^2}{\epsilon} n_x^{4/3},$$
(85)

where $\eta = \pi d^3 n_x/6$ is the packing factor of the hard spheres. This equation determines the critical temperature of exciton condensation

$$T_{\rm c} = \frac{16}{49} \left(\frac{2}{7}\right)^{1/3} \frac{\gamma I_{\rm a}}{2} \,, \tag{86}$$

the critical pressure

$$p_{\rm c} = \frac{1}{49} \left(\frac{2}{7}\right)^{1/3} \frac{\gamma I_{\rm a}}{2\pi} \left(\frac{\varepsilon I_{\rm a}}{e^2}\right)^3,\tag{87}$$

and the critical density

$$n_{\rm xc} = \frac{2}{7} \frac{3}{4\pi} \left(\frac{\varepsilon I_{\rm a}}{e^2}\right)^3. \tag{88}$$

According to Eqn (86), the critical temperature depends on the binding energy of excitons, but not on the dielectric constant of the semiconductor. In the limit of infinitely heavy holes, the binding energy estimated by Eqn (82) is $I_a \approx 30$ meV. Substituting this value of I_a into Eqns (86)– (88), we obtain the critical temperature $T_c \approx 21$ K, the pressure $p_c \approx 10^{-3}$ bar, and the density $n_c \approx 1.1 \times 10^{18}$ cm⁻³. These estimates agree reasonably well with the experimental data ($T_c = 24$ K, $n_{xc} \sim 10^{18}$ cm⁻³) [79].

To our knowledge, exciton condensation has only been observed in crystalline semiconductors [19]. Here, we estimate the critical point of exciton condensation in liquid xenon to show the predictive power of the dielectric model. The permittivity of liquid xenon is fairly well represented by the Clausius–Mossotti formula with the atomic polarizability:

$$\varepsilon = 1 + \frac{4\pi N \alpha_a}{1 - \varkappa} \,, \tag{89}$$

where $\varkappa = 4\pi N\alpha_a/3$. Substituting the polarizability $\alpha_a \approx 4 \times 10^{-24}$ cm⁻³ [30], and the atomic number density at the boiling temperature, $N = 1.6 \times 10^{22}$ cm⁻³ ($T_b = 165$ K), into Eqn (89), we find $\varepsilon \approx 2.1$ which is close to the optical permittivity 1.85 [80]. The permittivity determines the energy gap between the valence and conduction bands:

$$\Delta = I - \frac{e^2}{R_s} \left(1 - \frac{1}{\varepsilon} \right). \tag{90}$$

This is analogous to the energy gap in expanded fluid mercury defined by Eqn (76), except that at normal liquid density the percolation radius is replaced by the ordinary Wigner–Seitz cell radius. Estimating the energy gap with Eqn (90), one obtains 9.45 eV.

At normal density in liquid xenon, electrons of neighboring atoms can transfer to bare ions over the potential barrier, giving rise to a random walk of holes. Indeed, it can be directly verified that the top of the potential barriers, $U_{\rm m} = -2e^2/R_s$, is at about the atomic energy level, -I. As in ordinary semiconductors, electrons and holes created by the external excitation can occupy the exciton levels in the forbidden band.

Provided that the classically accessible electron radius is much greater than the Wigner-Seitz radius, the principal quantum number in the excitonic spectrum (80) must be limited to $n \ge 2$. There are excitonic peaks of 8.6 and 9.3 eV in the energy spectrum of liquid xenon, observed using photoconductivity [80]. Identifying these peaks with the excitation of n = 2 and 3 levels, respectively, we find the reduced mass to be close to the free-electron mass ⁵, and the energy gap 9.75 eV close to that estimated by Eqn (90).

In the limit of infinitely heavy holes $(m_h \ge m_e, m_e \approx m)$, we consider excitons as metastable atoms with the corresponding ionization potential $I_a = Ry/4\varepsilon^2 \approx 1$ eV. The lifetime of metastable atoms is limited by the nonadiabatic quenching with $\tau \sim R_s/vw \sim 10^{-6}$ s, where $v \approx 2 \times 10^4$ cm s⁻¹ is the thermal velocity of atoms, and $w \sim 10^{-6}$ is the probability of quenching [81].

Using Eqns (86)–(88), we obtain the following critical parameters

$$T_{\rm c} \approx 680 \text{ K}$$
, $p_{\rm c} \approx 3.9 \text{ bar}$, $n_{xc} \approx 1.4 \times 10^{20} \text{ cm}^{-3}$, (91)

i.e. the critical temperature is greater than that in silicon by almost 30 times, and the density by two orders of magnitude. We note that the critical temperature of exciton condensation is higher than the liquid – gas critical temperature of xenon ($T_c = 290$ K, $p_c = 58.3$ bar), therefore condensation of excitons is possible in gaseous xenon.

The exciton drops are somewhat like ball lightning, since at the critical point the stored exciton energy reaches 200 J cm⁻³. However, the exciton condensate is quickly damped because of exchange of the excitations between metastable atoms. The resonance process x + x = 0 + einvolving metastable atoms x with a great rate constant $Q_{xx} \sim 10^{-9}$ cm³ s⁻¹ produces atoms at the ground level 0 and hot electrons e which lose the energy in collisions with normal atoms. In the case of quasi-equilibrium exchange with the excitations $(n_x^2 = n_e N)$, where n_e is the density of hot electrons), the energy balance reduces to the equation for the density of excitons:

$$\frac{\mathrm{d}n_x}{\mathrm{d}t} = -K_{\mathrm{e}}n_x^2\,,\tag{92}$$

where $K_e = (2m/M)\sigma_{ea}v_e \approx 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ is the effective quenching rate constant, M is the atomic mass, $\sigma_{ea} \approx 3 \times 10^{-15} \text{ cm}^2$ is the cross section of electron scattering, and $v_e \approx 2 \times 10^8 \text{ cm s}^{-1}$ is the thermal velocity of electrons. According to Eqn (92), the lifetime of the exciton condensate, $(K_e n_x)^{-1} \sim 10^{-9}$ s, is much smaller than that of isolated excitons.

With its nonequilibrium nature, the exciton condensation is quite different from an ordinary liquid – gas phase transition. However, even in this case the plasma phase transition which occurs near the critical point is a continuation of the van der Waals condensation of excitons at lower densities.

14. Conclusions

The well-known van der Waals equation of state qualitatively describing the critical point of condensation in neutral fluids is still more suitable for Coulomb systems. Applying it to the model system of charged hard spheres, this equation is only to be modified by replacing a quadratic term describing the interatomic attraction with a renormalized Madelung energy having an exponent of 4/3, which represents the residual Coulomb interaction of the Bjerrum pairs. Besides, in plasma systems the additional pressure of partially free electrons walking between virtual atoms at thermal excitation energies is to be included. At the Coulomb critical points, the van der Waals description of the free volume becomes quite appropriate, since the packing factor of effective hard cores is much smaller than in neutral fluids. The residual Coulomb interaction is described in the mean field approximation which works better here than for the ordinary dispersion interaction between atoms. Therefore, a modified van der Waals equation of state for the Coulomb systems allows us to estimate quantitatively the critical points without extensive use of experimental parameters and with considerably better accuracy than using the original equation in the case of neutral fluids.

The Coulomb critical points are closely connected with the metal-insulator transition. A consequence of the proximity to the metal-insulator transition is a strong electron-ion coupling which excludes the possibility of using the perturbation theory. Therefore, one must include the electron-ion interaction from the beginning. The model of virtual atoms and Wigner-Seitz atomic cells seem to be the most suitable for this purpose. The interaction energy of virtual atoms versus the density, which is not sensitive to the electron structure due to averaging over different cells, is presented by a Madelung energy. A renormalized Madelung constant is up to 2.7 times smaller compared to the onecomponent plasma model which thus strongly overestimates the coupling energy.

It is characteristic of Coulomb critical points that the exchange repulsion radius of the atomic electron shells is smaller than the classically accessible radius. In this case, the core radius is determined by the bare Coulomb interior repulsion when the remainder ion of one atom enters the classically accessible sphere of another atom. Inversely, if the exchange repulsion radius is greater than the classically accessible radius, an expanded metal transfers into a semiconducting state still in the liquid phase.

In every case, the plasma phase transition with a Coulomb critical point is a continuation of the ordinary phase transition caused by attraction between neutral particles. The crossover to the ordinary transition and to the fluctuation critical region, as well as the question of whether the modified van der Waals equation has a range of applicability, still remain uninvestigated, though it seems not very actual.

The analysis shows that Coulomb critical points are determined by parameters which are not entirely universal and, for example, slightly vary for different metals. The calculation of all the parameters entering the equation of state for particular metals seems to require a much more sophisticated model describing the interaction of virtual atoms in percolation clusters. However, it is obvious that any such model must take into account the continuous spectrum of atomic excitations caused by collective screening of the remainder ions.

⁵ Asaf and Steinberg [80] supposed that the first peak corresponds to n = 1, and the second to the ionization threshold estimated to be 9.22 eV. This interpretation leads to difficulties when compared to the excitonic spectrum; besides, the effective electron mass 0.27*m* seems too low for the liquid.

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